COMMONWEALTH OF AUSTRALIA
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Blackman, Bottle, Schmid, Mocerino and Wille, Chemistry, 2007 (John Wiley)
ISBN: 9 78047081 0866
A/Prof Sébastien Perrier
Room: 351
Phone: 9351-3366
Email: s.perrier@chem.usyd.edu.au

Prof Scott Kable
Room: 311
Phone: 9351-2756
Email: s.kable@chem.usyd.edu.au

A/Prof Adam Bridgeman
Room: 222
Phone: 9351-2731
Email: a.bridgeman@chem.usyd.edu.au
Equilibrium and thermochemistry in industry

The winning of metals from ores

- Separating mineral from rock (flotation, etc)
- Converting ore to useful compound (roasting sulfides, etc)
- Converting oxide to metal
  - Ellingham plot
  - Equilibrium processes, Le Chatelier’s Principle at work
- Example, Copper
- Example, Steel
This lecture...

- Chemical manufacture (look at top 10)

We will use our knowledge of thermochemistry and equilibrium to investigate how these chemicals are produced.
## Top ten chemicals (US production)

<table>
<thead>
<tr>
<th>Rank</th>
<th>Chemical</th>
<th>Formula</th>
<th>Amount (million tonnes)</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfuric acid</td>
<td>$H_2SO_4$</td>
<td>41</td>
<td>fertilizers, chemicals, ...</td>
</tr>
<tr>
<td>2</td>
<td>Nitrogen</td>
<td>$N_2$</td>
<td>36.3</td>
<td>inert atmosphere</td>
</tr>
<tr>
<td>3</td>
<td>Oxygen</td>
<td>$O_2$</td>
<td>33.1</td>
<td>steel, medical, ...</td>
</tr>
<tr>
<td>4</td>
<td>Ethylene</td>
<td>$C_2H_4$</td>
<td>25.4</td>
<td>plastics, ...</td>
</tr>
<tr>
<td>5</td>
<td>Calcium oxide (lime)</td>
<td>CaO</td>
<td>20.6</td>
<td>metallurgy, (last lecture)</td>
</tr>
<tr>
<td>6</td>
<td>Ammonia</td>
<td>$NH_3$</td>
<td>17.2</td>
<td>fertilizers, chemicals, ...</td>
</tr>
<tr>
<td>7</td>
<td>Propylene</td>
<td>$C_3H_6$</td>
<td>13.2</td>
<td>plastics, ...</td>
</tr>
<tr>
<td>8</td>
<td>Phosphoric acid</td>
<td>$H_3PO_4$</td>
<td>12.5</td>
<td>fertilizers, ...</td>
</tr>
<tr>
<td>9</td>
<td>Chlorine</td>
<td>$Cl_2$</td>
<td>12.1</td>
<td>plastics, paper, ...</td>
</tr>
<tr>
<td>10</td>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>10.4</td>
<td>chemicals, soaps, ...</td>
</tr>
</tbody>
</table>

Ref: Petrucci, Harwood and Herring, p.128
# Top ten chemicals (US production)

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**How are they produced?**

- **from sulfur and smelting waste**
- **Distillation from air**
- **Petrochemical cracking**
- **from calcium carbonate**
- **Haber process, from $\text{N}_2$ and $\text{H}_2$**
- **from phosphate ores**
- **Electrolysis**
Sulfuric acid was certainly known to the alchemists (oil of vitriol) and it was the first chemical to be produced on an industrial scale. Sulfuric acid is made in greater volume than any other chemical in the world. The main uses of sulfuric acid today are:

- 61% Chemicals and dyes
- 19% Fertilizers
- 6% Steel work
- 4% Rayon
- 2.5% Pigments
- 1% Miscellaneous

Data:
H&C, p.660

Good ref: http://www.enviro-chem.com/plant-tech/3rdtier/acidprocess.html
1700: Burning sulfur with potassium nitrate (saltpeter) in glass bell jars. KNO₃ was a catalyst, unbeknownst to the producers. SO₂(g) reacts with water in jar to make dilute H₂SO₄.

1746: Roebuck invented the “lead-chamber process” where lead was used instead of glass as the only known metal then known to be resistant to H₂SO₄ (manufacture = 100 lbs). Variants of this process are used to this day, although decreasing because of the environmental issues with lead.

1827: Gay-Lussac improves lead-chamber process by using towers, through which air was blown (more O₂), and from which NOₓ gases could be recycled to save on the cost of the KNO₃ catalyst. Maximum strength of 78% purity by distillation of weak acid.

1831: Phillips patents a catalytic method to produce sulfur trioxide using platinum catalyst. Expensive and small scale, but up to 98% “fuming sulfuric acid” could be produced. First plant established in 1875.
Manufacture of sulfuric acid

Three type of $\text{H}_2\text{SO}_4$ plants:

1. Sulfur burning
   - A plant for the primary production of sulfuric acid.

2. Spent acid regeneration
   - An SAR plant reconcentrates acid to usable strength.

3. Metallurgical plant
   - A metallurgical plant uses toxic waste $\text{SO}_2$ gases from smelting of metal (see last lecture) and converts them into sulfuric acid

Let’s look at the chemistry involved…
Chemistry of sulfuric acid

**Step 1: Preparation of SO$_2$**

- This is where the three methods of manufacture differ.

Sulfur burning:

$$S(l) + O_2(g) \rightarrow SO_2(g) + \text{heat}$$

Spent acid regeneration:

$$H_2SO_4 (aq) + H_2S(g) + O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l)$$

Metallurgical plant:

$$MS(s) + 1.5O_2(g) + \text{heat} \rightarrow MO(s) + SO_2(g)$$

where MS and MO are a metal sulfide and oxide respectively, as in last lecture.
Step 2: Preparation of $SO_3$

- This is the heart of modern manufacture. The original catalyst was platinum, now vanadium pentoxide is used.

Catalytic conversion of $SO_2$ to $SO_3$:

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g) + \text{much heat}$$

Too much heat production is a problem... (Why?)

So this process is done in stages, where the heat is removed at every stage, and recycled, e.g. to produce heat for first stage of metallurgical plant.
Step 3: Absorption of SO$_3$

This is where conc. or fuming sulfuric acid is made

Reaction of SO$_3$ with water (usually with weaker H$_2$SO$_4$)

$$\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{SO}_4(\text{l}) + \text{heat}$$

In practice, the sulfuric acid is recycled through the system, getting stronger and stronger each time, until reaching 98-99% purity. Again, the heat must be controlled.
Western Mining Corporation Fertilizers Ltd built one of the world’s largest metallurgical sulfuric acid plants at Mt Isa, NW Qld in 1999. Capable of 1.2 Mtpa.

The complex consists of the following:
- 300 tonne/hr beneficitation plant.
- 1500 tonne/day phosphoric acid plant.
- 600 tonne/day ammonia plant
- 135 tonne/day granulation plant.

Western Mining Corporation opened a plant at Kalgoorlie in 1997. Capable of producing 500 000 tonnes per year.

Pasminco’s Risdon plant in Tasmania being opened.

Southern Copper smelter and refinery at Pt Kembla, NSW, closed in 1995 but reopened in 1999 near-doubling its associated sulfuric acid capacity. Closed in 2003 under its new Japanese ownership.
Bacteria provide nature's way of "fixing" nitrogen - an essential element for life. About 13% of all N-fixation is accomplished industrially, using the Haber process. Over 110 million tonnes are produced worldwide - making it the largest produced chemical on a mole basis. The main uses of ammonia today are:

- Nitric acid: 79%
- Fertilizer: 5.9%
- Nylon: 5%
- Chemicals: 2%
- Miscellaneous: 7.9%

Data: Silb., p.744

Goodrefs: Any general chemistry text will have info about the Haber cycle.
Nitrogen biocycle

Nitrogen is one of the essential "life elements".

Amino acid

\[
\begin{align*}
H_2N-C-C-OH & + \ H-N-C-COH \\
\rightarrow & \ H_2N-C-C-N-C-C-COH
\end{align*}
\]

Peptide linkage

R = one of 20 different organic groups:
- e.g. alanine, R = CH\(_3\) or cysteine, R = CH\(_2\)SH

98\% of all elemental N, at sea level, is found as N\(_2\).
Yet N is found in all living organisms. How does N work its way around the ecosystem?
Nitrogen gets into the soil for plants to use by:

(Nitrification)

- nitrates (NO$_3^-$) rained out from air
  - Nitrates formed in air from pollution or lightning
  - N$_2$ + O$_2$ $\rightarrow$ 2 NO;
  - NO oxidised to NO$_2$ (see previous lecture)
  - NO$_2$ taken up into clouds $\rightarrow$ HNO$_3$

- N$_2$-fixing bacteria
  - In soil or in root nodules (leguminous plants)
  - N$_2$(g) + 8 H$^+$(aq) + 6 e$^-$ $\rightarrow$ 2 NH$_4^+$(aq)

Bacterial nodule on pea root
Nitrogen biocycle

Nitrification (continued)

Nitrogen gets into the soil for plants to use by:

- mineralisation
  - Soil bacteria convert soil nitrogen (organic) into \( \text{NH}_4^+ \)
  - Organic N \( \rightarrow \rightarrow \rightarrow \) \( \text{NH}_4^+ \)

- nitrogen fixation
  - Stage 1: \( \text{NH}_4^+(aq) + 1.5\text{O}_2(g) \rightarrow \text{NO}_2^-(aq) + 2\text{H}^+(aq) + \text{H}_2\text{O}(l) + \text{energy} \)
  - Stage 2: \( \text{NO}_2^-(aq) + 0.5\text{O}_2(g) \rightarrow \text{NO}_3^-(aq) + \text{energy} \)

- fertilizers
  - Organic (manure, etc)
  - Inorganic (nitrogen salts, e.g. \( \text{NH}_4\text{NO}_3 \))
  - \( \text{N}_2(g) + 8\text{H}^+(aq) + 6\text{e}^- \rightarrow 2\text{NH}_4^+(aq) \)
Nitrogen gets returned to the atmosphere by:

(Denitrification)

- Decaying organic matter
  - Sewage, crop waste, animal waste → $\text{NH}_3(g)$
- Denitrifying bacteria
  - $\text{NO}_3^-(aq) \rightarrow \text{NO}_2^-(aq) \rightarrow \text{N}_2\text{O}(g) \rightarrow \text{N}_2(g)$
Why is ammonia so important? It’s the starting point for many processes:
- fertilizers (N-biocycle)
- explosives (L.23)
- Fuels (L.23)
- polymers (e.g. nylon, L.37)
- HNO₃

\[
N_2(g) + 3 \ H_2(g) \ \Leftrightarrow \ 2 \ NH_3(g)
\]
But \( N_2 \) is so stable... how?
Haber, 1909  Bosch, 1913

Haber synthesised 100g in 1909
Bosch scaled up for industry, 1913.
Now 110 million tonnes per year produced

Fritz Haber

Haber, Nobel Prize, 1918
Bosch, Nobel Prize, 1931

Haber’s original experimental apparatus
Equilibrium

$N_2(g) + 3 \, H_2(g) \rightleftharpoons 2 \, NH_3(g) + 91.8 \, kJ$

How do you think the production of $NH_3$ could be optimised?

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$K_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>$7.2 \times 10^{15}$</td>
</tr>
<tr>
<td>300</td>
<td>$2.7 \times 10^8$</td>
</tr>
<tr>
<td>400</td>
<td>$3.9 \times 10^4$</td>
</tr>
<tr>
<td>500</td>
<td>172</td>
</tr>
<tr>
<td>600</td>
<td>4.53</td>
</tr>
<tr>
<td>700</td>
<td>0.30</td>
</tr>
<tr>
<td>800</td>
<td>0.040</td>
</tr>
</tbody>
</table>

Eq'm shifts to the LEFT
Increasing yield of NH$_3$

- Remove NH$_3$
- Increase pressure
- Decrease temperature

**Thermodynamics**

- Too slow at low temperature
- Use a catalyst

**Kinetics**
Increasing yield of NH₃

- Increase pressure (within reason)
- Use a catalyst
- Remove NH₃
- Intermediate temperature (compromise)

How?

Industrial Conditions:
- ~400°C
- 70-200 atm
- ~40% yield
N\textsubscript{2} and H\textsubscript{2} are compressed and enter the reaction chamber.

NH\textsubscript{3} and unreacted N\textsubscript{2} and H\textsubscript{2} leave the chamber. The NH\textsubscript{3} is condensed, and the unreacted N\textsubscript{2} and H\textsubscript{2} return to the reaction chamber.

Figure 14.15 Blackman
Schematic of Industrial Process

Haber's original experimental apparatus:
About 12.5 million tons of phosphoric acid, $H_3PO_4$, are produced in the US annually. Most of the acid is used in the production of fertilizers, with the remainder being used for detergent additives, cleaners, insecticide production, and cattle feed additives. The commercial method of preparation is the addition of sulfuric acid to phosphate rock.

$3 \ H_2SO_4(\ell) + Ca_3(PO_4)_2(s) + 6 \ H_2O(\ell) \ \Rightarrow \ 2 \ H_3PO_4(s) + 3 \ CaSO_4\cdot2H_2O(s)$

![Pie chart showing uses of phosphoric acid]

Source: scifun.chem.wisc.edu/CHEMWEEK/chemweek.html?Slide 25-27
The sulfuric acid manufacturing plant mentioned earlier exists as part of a complex to provide sulfuric acid for phosphate production.
Albright & Wilson (Australia) Limited's Yarraville site produces phosphoric acid and a wide range of technical and food grade phosphates and polyphosphates made from imported elemental phosphorus or wet process phosphoric acid.

These products find application in such diverse industry groups as detergents, food products and processing, metal finishing, mining and mineral processing, pharmaceuticals, crop care and water treatment.

Located in the Melbourne suburb of Yarraville, the manufacturing site is situated on the banks of the Maribyrnong River where the Company began production of phosphoric acid and food phosphates over 60 years ago.
Ethylene and propylene are both made from “cracking” hydrocarbons in the petroleum industry. By far their greatest use is in the manufacture of polymers (plastics). We shall discuss polymers later this semester.

Source: H&C, p.824
#9&10 Chlorine / NaOH

Chlorine \((\text{Cl}_2)\) and sodium hydroxide are produced in the same process, involving electrolysis of common sea salt. We will look at electrolysis in the next topic.

\[
2 \text{Na}^+(aq) + 2 \text{Cl}^-(aq) + 2 \text{H}_2\text{O}(l) \rightarrow \text{Cl}_2(g) + \text{H}_2(g) + 2 \text{Na}^+(aq) + 2 \text{OH}^-(aq)
\]

**Uses of chlorine**
- PVC: 34%
- Isocyanates/oxygenates: 26%
- Inorganic chemicals: 13%
- Chloromethanes: 7.1%
- Epichlorohydrin: 4%
- Solvents: 4%
- Miscellaneous: 4.1%

**Uses of sodium hydroxide**
- Soaps and detergents: 28%
- Pulp and paper: 26%
- Inorganic chemicals: 13%
- Organic chemicals: 4%
- Water treatment: 3%
- AI manufacture: 4%
- Miscellaneous: 22%

Source: www.eurochlor.org

Source: H&C, p.597 Slide 25-31
Example questions

CONCEPTS

- Control of equilibrium in industrial processes.
- Energy recycling
- Endo- and exothermic processes in industry
- Methods of manufacture of $\text{H}_2\text{SO}_4$ and $\text{NH}_3$
- Uses of these chemicals

CALCULATIONS

- Industrial-type equilibrium and thermochemistry problems